Laser ablation of aluminum at 193, 248, and 351 nm

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Pulsed laser ablation of an aluminum target at 193, 248, and 351 nm has been investigated by laser-induced fluorescence (LIF) spectroscopy. Velocity distributions of the ablated Al atoms have been measured directly by monitoring their flight times from the target to the probe laser beam, and by Doppler laser spectroscopy. The velocity distributions resulting from the three wavelengths can all be characterized as hyperthermal, with average velocities of between 4.5×10^5 and 6.5×10^5 cm/s over a fluence range of 0.3–6.5 J/cm^2. Average values of the Al atom distribution can also be derived by measuring the AlO internal energy distribution of the "hot" Al atom reaction with low pressures of O_2. For excimer laser ablation of aluminum at 248 nm, we have found an average Al atom velocity of $>2 \times 10^5$ cm/s. Possible mechanisms for the production of these hyperthermal velocity distributions are discussed.

Pulsed laser deposition methods are emerging as some of the leading techniques for producing thin films of varying compositions.[1,2] The technique has been applied to the fabrication of high-temperature superconducting and semiconductor films of complex composition, and is particularly useful because of the retention of stoichiometry in going from the laser target to the thin film.[3,4] Recent developments have demonstrated the need for stringent stoichiometric requirements in the new materials. In spite of the expanding applications, the mechanism of the laser ablation process remains poorly understood.[3]

Group III metals maintain a strong presence in the new semiconductor technology, with aluminum playing an increasingly important role in the latest devices.[5] Furthermore, aluminum has recently found its way into the superconductor area, particularly in the new superconducting tunnel junctions, which are produced by successive deposition of Nb and Al films.[6] With the increasing appearance of new technologies utilizing laser ablation/laser deposition methods to produce aluminum thin films, a clearer understanding of the underlying physical mechanisms are necessary. We report here a characterization of the kinetic energies of aluminum atoms following laser ablation of a flat metal disk by using laser-induced fluorescence (LIF) as a probe.

The apparatus used for these experiments has been described previously.[7] Aluminum atoms are produced by laser ablation of a machined flat 1-in.-diam disk mounted on the shaft of a rotary motion feedthrough with an adjustable nylon coupler, which is slowly rotated (~ 6 rpm) to prevent drilling a hole in the aluminum flat. The ablation laser for the reported data is a Lambda Physik excimer laser (model LPX 205i), operating on the ArF, KrF, or XeF excimer transitions at 193, 248, or 351 nm, respectively, which is focused to a point onto the aluminum surface with either a 150 mm f.l. or 250 mm f.l. Suprasil quartz lens. The spot size of the focused laser beam is 1–4 mm^2. Laser

fluences were varied from 300 to 6500 mJ/cm^2. The direct production of both excited and ground states of Al has been confirmed by emission and laser-induced fluorescence spectroscopy, respectively.[7,8] In order to characterize the kinetic energy of the ground state aluminum atoms present, we employ three methods. First, we monitor the Al atoms directly by exciting the $4^2S \leftarrow 3^2P_{1/2}$ transition centered near 394.4 nm and monitoring the $4^2S \rightarrow 3^2P_{3/2}$ fluorescence through a narrow bandpass filter at 396.2 nm.[9] The probe laser (for all methods) is a Lambda Physik FL3002 tunable dye laser (full width at half maximum $= 0.2$ cm^{-1}) pumped by a XeCl excimer laser (Lambda Physik LPX 205i) operating at 308 nm. The dye laser beam is directed down the length of the cell, and passes within 1–3.5 mm of the rotating flat and intersects the focused vaporization laser. The fluorescence is observed with a high gain photomultiplier, at 90° relative to both the probe and the ablation lasers, through a sapphire window. The excimer-pumped dye laser can be fired at variable delay times relative to the vaporization laser by using a digital delay generator. Time-of-flight measurements are obtained by measuring the intensity of the atomic fluorescence signal as a function of delay time with the probe laser at a fixed distance from the metal disk. Delay times are typically varied from 50 ns to 5 μs.

Typical velocity distributions of the Al atoms following 248 and 351 nm laser ablation of an aluminum target are shown in Fig. 1. The velocity distributions are dependent upon the vaporization laser fluence, but those displayed in Fig. 1 are obtained under very similar conditions of fluence and focusing. Also shown in Fig. 1 is a Maxwellian velocity distribution of Al atoms (solid line) assuming a temperature of 72 000 K ($kT = 6.2$ eV). We cannot accurately fit any of our experimental data with Maxwellian velocity distributions, and the solid line is shown in Fig. 1 only as a frame of reference. We conclude that the velocity distributions are non-Maxwellian.

Due to the high kinetic energy content of the Al atoms, we were also able to confirm the average velocities by Doppler spectroscopy. In this case, the atomic transition was

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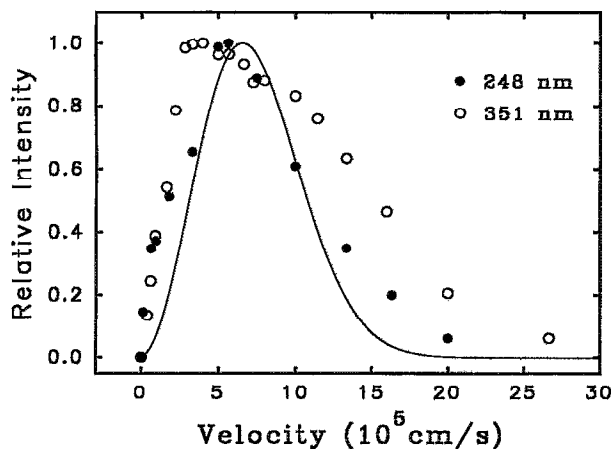
FIG. 1. The velocity distribution of the Al atoms following excimer laser ablation at 248 nm (●) and 351 nm (○). The solid line represents a Maxwellian distribution of Al atoms at a temperature of 72 000 K, as a reference.

scanned at a particular delay time, and the spectrum was recorded. For these experiments, the output of the photomultiplier is signal averaged with a gated integrator/microcomputer system for spectroscopic identification. Typical shot-to-shot fluctuations of the fluorescence signal are 10–20%. The laser-induced fluorescence spectrum of the $4^2S \leftarrow 3^2P_{1/2}$ transition of Al is shown in Fig. 2. The spectrum was obtained at a delay time of 500 ns following the 248 nm ablation of the metal target (corresponding to the peak of the velocity distribution in Fig. 1). The measured widths ($\Delta\lambda = 0.0145$ nm; $v \sim 4.7 \times 10^5$ cm/s) were in good agreement with the velocity distributions measured by the time of flight method.

In the third method used for characterizing the kinetic energy of the ablated Al atoms, we encourage the production of AlO by introducing trace quantities of O_2 (0.03–1.00 Torr) into the reaction vessel. The AlO is detected by

FIG. 2. The Doppler profile of the Al($4^2S \leftarrow 3^2P_{1/2}$) transition obtained at a delay of 500 ns between the excimer laser (248 nm) and the probe laser. $\Delta\lambda$ corresponds to the full width half maximum used for the velocity measurement. The probe laser was 2 mm from the metal ablation target.
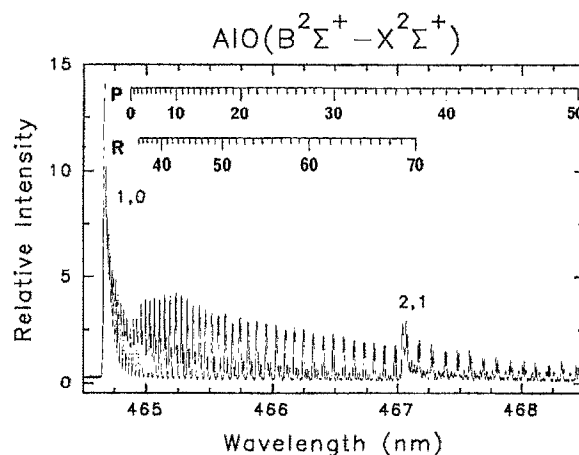

FIG. 3. LIF spectrum of the AlO($B^2\Sigma^+ - X^2\Sigma^+$) transition obtained following excimer laser ablation of Al at 248 nm in the presence of a trace amount of O_2. The spectrum was obtained under the following conditions: $P_{O_2} = 0.200$ Torr, delay time $= 2$ μs.

LIF of the B–X (1,0) transition near 465 nm. No AlO laser-induced fluorescence is observed unless O_2 is added to the cell, confirming that we are ablating Al and not a thin film of Al_2O_3. A typical LIF spectrum of AlO $B^2\Sigma^+ - X^2\Sigma^+$) obtained with our apparatus is shown in Fig. 3. This spectrum and others can be analyzed to obtain a rotational temperature, which is characteristic of the time delay and total pressure in the cell. We have been able to measure a LIF spectrum with a sufficient signal-to-noise ratio at an O_2 pressure of 0.06 Torr and 2 μs delay between the ablation and the probe lasers to obtain a rotational temperature. If we assume an equilibrium 298 K gas, this corresponds to an average hard sphere collision frequency of $\sim 5 \times 10^6$ (Torr s)$^{-1}$, or about 0.5 collisions. The rotational temperature measured from this LIF spectrum corresponds to 1440 K. Pasternack and Dagdigian have investigated the reaction dynamics of $Al + O_2 \rightarrow AlO + O$ by measuring the internal energy of the diatomic (AlO) product as a function of the average kinetic energy of the atomic (Al) reactant.[10] Their results indicate that an increase in the Al atom velocity increases the product rotational temperature. Based on these results, Al atom velocities of $> 2 \times 10^5$ cm/s are required to produce the AlO rotational temperatures observed here. This result demonstrates a consistency with our time-of-flight and Doppler profile measurements, and shows that internal energies can be used to approximate kinetic energies in a system with well-characterized dynamics.

As can be seen from our data (cf. Figs. 1 and 2), the kinetic energy of the Al atoms resulting from the ablation is high. Dreyfus et al. have previously investigated the excimer laser ablation of alumina, Al_2O_3.[11] Their results provided strong evidence that the vaporization of Al and AlO from alumina was not a thermal mechanism (defined as an equilibrium process at the surface) leading the authors to conclude that an electronic process must be operative. In the experiments on the laser ablation of alumina, kinetic energies of ~ 4 eV were found for the atomic aluminum
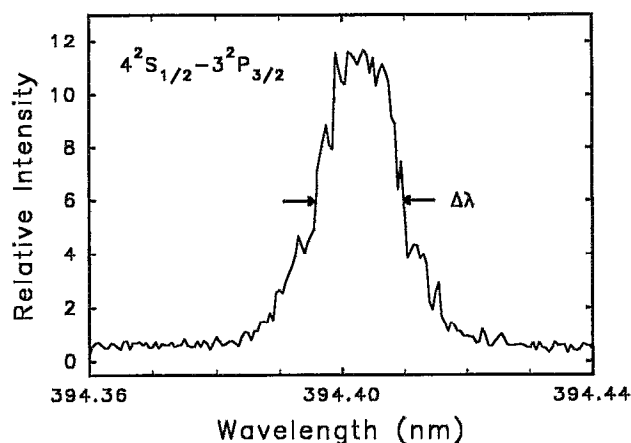
near threshold, which increased drastically to 20 eV for high laser fluences (~ 3 J/cm^2). In our experiments, the average kinetic energies of the Al atoms are slightly higher, ~ 5 eV, at threshold, but only increase to about 6 eV at higher laser fluences (~ 6 J/cm^2). This supports our hypothesis that we are indeed ablating Al metal and not a thin film of Al$_2$O$_3$ on the surface.

The mechanism by which the Al atoms obtain their high velocities is not clear. In the limiting case of pure thermal "vaporization" at the surface, it would be expected that the atoms would come off near the critical temperature (~ 3940 K) of aluminum.[12] If the Al atoms come off the surface by a thermal mechanism, the particle velocities should be described by a half-range Maxwellian distribution.[13] In this case, only positive velocities normal to the target are considered, and the surface temperature T_s is characterized by $kT_s = E/2$, where E is the average of the TOF distribution. By using the kinetic energy peak in our experiments at 248 nm, this equation predicts a surface temperature of $\sim 34\,000$ K. Kelly and Dreyfus[13] have recently shown that surface temperatures can be overestimated by this equation, and show that for on-axis measurements, $T_s = E/\eta k$ is a better estimate where $\eta = 2.52$ for monoatomic species, due to the formation of a Knudsen layer. For this case, the surface temperature is only reduced to $\sim 27\,000$ K. Since the critical temperature is closer to 3940 K, these surface temperatures are unlikely. The surface temperature rise of the target has been previously estimated to be on the order of several hundred degrees Kelvin.[11]

A more likely explanation for the production of the hyperthermal velocity distributions is that some type of nonequilibrium mechanism is involved. This is supported by the inability to fit our data with a Maxwellian distribution and the direct production of excited state Al atoms. Two other possibilities that may explain our results are: (1) subsurface explosions, where subsurface temperatures are significantly higher than the surface during the laser pulse causing the explosive removal of material from the target,[14] or (2) inverse bremsstrahlung, where the particles are excited to higher kinetic energy by absorption of radiation generated above the surface.[15] The inverse bremsstrahlung process, while commonly postulated for ionic systems, would most likely impart much more kinetic energy than we are observing.

In conclusion, we have reported in this letter three techniques by which the kinetic energy of atoms ablated from a metal target can be characterized. All three of these techniques provide consistent results, with each of them having certain advantages. The time-of-flight technique can provide the entire velocity distribution in a direct, rapid manner, but requires an accurate knowledge of the beam positions. This limitation is absent in the Doppler laser spectroscopy method, but obtaining an entire distribution by this method is tedious. Furthermore, when using typical commercial lasers (spectral resolution ~ 0.2–0.5 cm^{-1}), this technique will only work for species with high kinetic energies. The third method, in which the high velocity species is allowed to react, and the subsequent product internal state distributions are measured, has advantages in minimizing the effects of particle-particle collisions near the surface of the target by "capturing" the atom. However the technique requires a detailed knowledge of the dynamics of the system being employed. Further work, ongoing in our laboratory, is still required to completely understand the mechanisms of the laser ablation of aluminum metal.

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